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MACROMOLECULAR ANTIOXIDANTS USUALLY IGNORED, ARE THE MAJOR PART OF DIETARY POLYPHENOLS: A STUDY IN THE GRAPES INDUSTRIAL RESIDUES

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ABSTRACT

This work aims to determine the concentration of phenolic compounds in different grape residue varieties generated by juice industry in the São Francisco Valley, as well as to evaluate macromolecular antioxidant compounds in grape residue with presenting as a main scope the realization of a detailed study on the properties of this product, seeking to identify it and characterize it as a commercial product rich in macroantioxidants. In this research, bagasse (husks + seeds) from the juice industry, obtained after the pressing and filtration stages during the production process, were analyzed. The results showed high levels of macroantioxidants compounds and polyphenols for the grape residue, associated to the antioxidant activity, and expressed in mean values ± standard deviation. It can be concluded that industrial grape residue, especially from the production of juices, are rich in macroantioxidants and can be used by food industry as a bioactive.

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INTRODUCTION

The social increasing demand for natural products that contribute to improvement of the quality of life, along with the industrial sector's concern in effort to meet this demand, has driven studies in the search for new technologies, aiming to health promotion and, at the same time, the reduction of economic losses and the impact of industrial activity on the environment (Melo, 2010). All over the world, and especially in Brazil, which has its economy heavily based on agribusiness, large amounts of waste are generated by food processing industries (Makris *et al.,* 2007), which despite being considered serious environmental problems, can be in many cases rich sources of bioactive compounds, including antioxidant and antimicrobial substances (Rubilar *et al.,* 2007). Grape and its agroindustrial residues are an important source of bioactive phenolic compounds, represented mainly by flavanols (catechins and epicatechins), anthocyanins, resveratrol, quercetin and kaempferol (Dani *et al.,* 2007; Souza, 2008). By-products obtained after the exploitation of grapes, consisting of husks and seeds, are a very inexpensive source for the extraction of phenolic compounds, which can be used in dietary supplements, herbal products, cosmetics and as natural antioxidants in food industry (Arvanitoyannis *et al.,* 2006). Thus, both grape and its bagasse constitute an important natural source of phenolic compounds, which can be characterized as a product of high antioxidant potential, capable of combating oxidative processes and yet with the additional advantage of presenting a considerable content of dietary fiber antioxidant and unsaturated fatty acids, nutrients whose consumption is related to numerous beneficial physiological effects (Llobera & Cañellas, 2007). In this way, the definition of this residue is necessary for its use by food industry as a natural source of antioxidants and with a low cost of acquisition (Shojaee-Aliabadi *et al.,* 2013). The so-called macromolecular antioxidants, found in grape residue, have a high biological and antioxidant activity and exhibit promising

properties related to health (Saura-Calixto, 2017), especially in relation to gastrointestinal (including colorectal) and cardiovascular health (Pérez-Jiménez *et al.,* 2013).

MATERIAL AND METHODS

Industrial grape residue acquisition: The grape residue used in this study was provided by agroindustries located in the São Francisco Valley, Brazil. Samples were collected during a period of regular operation of companies, according to availability of varieties over the year 2015.

Preparation of extracts: The extracts for analysis of phenolic compounds and evaluation of the antioxidant activity were conducted according to methodologies described by Rufino *et al*. (2007a) and Rufino *et al.* (2007b), which are works referenced in several focus studies in analysis of bioactive compounds in tropical fruits. Initially, the extraction was performed by adding 20 mL of methanol (50:50 v/v) to grape residue. Then, the solution was homogenized in vortex and allowed to stand for 60 minutes at room temperature. The extraction was proceeded by using the centrifuge at 11.000 rpm for 20 minutes and the supernatant 1 was collected and stored in a 50 mL volumetric flask. To the precipitate, 20 mL of a second acetone extracting solution (70:30 v/v) was added, standing for a further 1 hour under light protection, then homogenized and centrifuged at 11.000 rpm for 20 minutes. The second supernatant obtained was mixed to the first one in the same 50 mL flask, which was checked with distilled water, obtaining the extract for determination of extractable polyphenols. The extracts were then transferred to an amber glass container, where they were stored away from light and finally the extracts were packed under refrigeration.

Determination of content of total extractable polyphenols

The extractable polyphenols were determined by the Folin-Ciocalteau method, using gallic acid as standard, according to the methodology described by Larrauri *et al.* (1997) and adapted by Rufino *et al.* (2007). In glass cartridge, 50 µL aliquots of the extracts (supernatants) were added, and distilled water was added to make up the volume to 0,5 mL. 0,5 mL of the Folin-Ciocalteau reagent, 1,0 mL of 20% Na_2CO_3 and 1,0 mL of distilled water were then added. The glass cartridge was homogenized and allowed to stand for 30 minutes. A white reagent was conducted in same conditions and an analytical curve containing 50, 40, 30, 20, 10 µg. mL^{-1} gallic acid was constructed. The reading was performed in a spectrophotometer at 700 nm, using as reference the standard curve of gallic acid. The results were expressed as mg of gallic acid per 100 g^{-1} of sample.

Determination of grape residue antioxidant activity: Several analytical techniques have been used to determine antioxidant activity *in vitro* in order to allow a rapid selection of substances and/or mixtures of bioactive compounds that are important in promoting health (Pulido *et al.,* 2000). Among the most used methods are the reduction of free radical DPPH• (2,2-diphenyl-1-picryl-hydrazyl radical) and reduction of the radical $ABTS^+$ [2,2-azino-bis (3-ethyl-benzothiazoline-6-sulfonic acid)] (Rufino *et al.,* 2007a; Rufino *et al.,* 2007b). The DPPH method is based on measuring the antioxidant capacity of a substance in sequestering the DPPH radical, reducing it to 2,2-diphenylpicrilhydrazine to give a yellow color solution. By decreasing absorbance, the amount of the DPPH radical that is consumed by antioxidant or percentage of the DPPH free radical remaining in reaction medium is determined (Brand-Williams et al., 1995; Rufino *et al.,* 2007b). The ABTS radical method consists in generation of blue-green $ABTS^{\bullet+}$, by means of the reaction of stock solution of ABTS with potassium persulfate. With addition of an antioxidant occurs reduction of $ABTS^+$ to ABTS promoting loss of coloration of reaction medium. With extent of color loss, the percent inhibition of $ABTS^+$ is determined as a function of Trolox (6-hydroxy-2,5,7,8-tetramethylchromo-2-carboxylic acid), a standard subjected to same conditions of analysis of antioxidant (Re *et al.,* 1999).

Macroantioxidants content determination: The determination of macroantioxidants in plant foods requires several steps in order to remove low molecular weight phenolic compounds and other soluble substances, as well as to break macromolecules, especially those associated with proteins and polysaccharides. The MACAN content was determined according to the methodology suggested by Pérez-Jiménez & Saura-Calixto (2015).

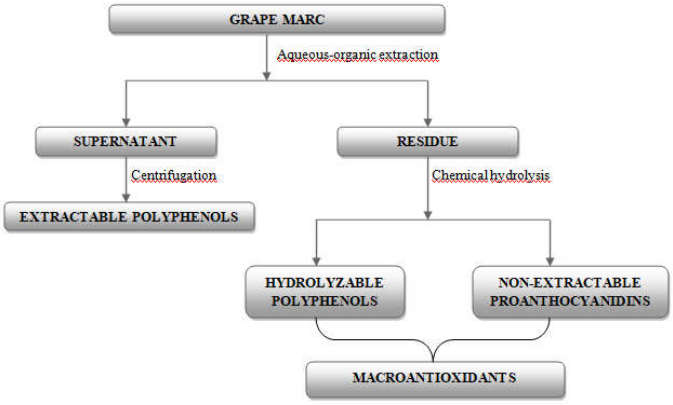

Figure 1. Schematic of the usual procedure for the analysis of non-extractable macroantioxidants or polyphenols (Pérez-Jiménez & Saura-Calixto, 2015).

A chemical extraction with organic hydroalcoholic solvents (50% methanol and 70% acetone) was conducted on grape residues, which releases the EPP (extractable polyphenols) content in supernatant fraction and produces a precipitate. The precipitate is then subjected to chemical hydrolysis, performed in two steps, in order to release the content of HPP (hydrolyzable polyphenols) and NEPA (non-extractable proanthocyanidins) from grape residue. The hydrolysates obtained after these treatments were then analyzed using spectrophotometric techniques (Pérez-Jiménez & Saura-Calixto, 2015).

Statistical Analysis: The determinations were performed in triplicate and the results were expressed as mean ± standard deviation.

RESULTS

Table 1 presents results for determination of total extractable polyphenols from extracts elaborated from grape residues as of pressing and filtration stages during juicing process. The content of total extractable polyphenols in the hydroalcoholic extracts of grape residues ranged from 151.89 to 357.32 mg GAE/g.

Table 1. Determination of total extractable polyphenols from elaborated extracts of grape residues [a].

Varieties of grape residue	Total Extractable Polyphenols (mg gallic acid/100g sample)
Isabel Early (1st cycle) – initial stage	231.42 ± 15.53
Isabel Early (1st cycle) – final stage	228.21 ± 4.51
BRS Magna (1st cycle) – initial stage	357.32 ± 23.13
BRS Magna (1st cycle) – final stage	151.89 ± 19.06
Isabel Early + BRS Violet (1st cycle) – initial stage	284.39 ± 4.83
Isabel Early + BRS Violet (1st cycle) – final stage	155.55 ± 14.92
BRS Magna (2nd cycle) – final stage	151.95 ± 11.25

[a]Mean value ± standard deviation, n = 3.

Table 2. Values for the determination of antioxidant activity by the DPPH and ABTS methods of the elaborated extracts of grape (dry matter)[a]

Varieties of grape residue	DPPH (g fruit/g DPPH)	ABTS (μM trolox/g)
Isabel Early (1st cycle) – initial stage	0.14 ± 0.03	357.80 ± 19.15
Isabel Early (1st cycle) – final stage	0.58 ± 0.07	397.62 ± 29.31
BRS Magna (1st cycle) – initial stage	0.10 ± 0.02	860.84 ± 13.24
BRS Magna (1st cycle) – final stage	0.36 ± 0.02	460.68 ± 27.18
Isabel Early + BRS Violet (1st cycle) – initial stage	0.17 ± 0.02	661.24 ± 12.33
Isabel Early + BRS Violet (1st cycle) – final stage	0.27 ± 0.01	538.67 ± 11.48
BRS Magna (2nd cycle) – final stage	0.31 ± 0.01	529.53 ± 37.34

[a]Mean value ± standard deviation, n = 3.

Table 3. Determination of the content of macroantioxidants in the elaborated extracts of grape residues [a]

Amostras de uva	NEPP (mg /100g matéria seca)		
	HPP (mg/100g)	NEPA (mg/100g)	NEPP (mg/100g)
Isabel Precoce (1º ciclo)	271,22 ± 4,85	261,12 ± 3,40	532,34 ± 5,92
BRS Magna (1º ciclo)	284,63 ± 8,70	326,12 ± 5,29	610,75 ± 10,18
BRS Magna (2º ciclo)	282,74 ± 6,22	313,28 ± 3,87	596,02 ± 7,32
Isabel Precoce + BRS Violeta (1º ciclo)	280,36 ±12,81	289,74 ± 3,78	570,10 ± 13,36
Touriga (1º ciclo)	154,55 ± 18,92	309,13 ± 3,59	463,68 ± 19,26
Touriga (2º ciclo)	159,91 ± 3,79	293,89 ± 3,59	453,80 ± 5,22
Alicante Bouschet (1º ciclo)	236,97 ± 13,30	364,24 ± 0,18	601,21 ± 13,30
Alicante Bouschet (2º ciclo)	251,64 ± 2,49	309,53 ± 0,75	561,17 ± 2,60
Tempranillo (1º ciclo)	185,35 ± 1,92	360,63 ± 5,29	545,98 ± 5,63
Tempranillo (2º ciclo)	200,81 ± 13,64	273,69 ± 4,91	474,50 ± 14,50
Egiodolla (1º ciclo)	187,38 ± 3,08	362,77 ± 0,00	550,15 ± 3,08
Egiodolla (2º ciclo)	201,78 ± 6,62	350,06 ±17,96	551,84 ± 19,14

[a]Mean value ± standard deviation, n = 3.

In the first semester cycle, the varieties that showed highest concentration of polyphenols were observed in the residues of BRS Magna (1st cycle) - initial stage; Isabel Early + BRS Violet (1st cycle) - initial stage; Isabel Precoce (1st cycle) - final stage. In the second semester cycle, there was no significant change in the content of total extractable polyphenols as observed in the BRS Magna (2nd cycle) variety - final stage when compared to the first half production cycle of 2015, according to results expressed in Table 1. The data on the antioxidant activity of the hydroalcoholic extracts of residues from elaboration of grape juice by radical DPPH and $ABTS^{\bullet+}$ method is presented in Table 2. Among the grape varieties evaluated, the highest total antioxidant activity, determined by the DPPH method, in two production cycles was observed in BRS Magna (1st cycle) - initial stage with 0.10 g/g DPPH; Isabel Early (1st cycle) - initial stage with 0.14 g/g DPPH followed by Isabel Early + BRS Violet (1st cycle) - initial stage with 0.17 g/g DPPH to reduce free radicals by 50% of the solution. Table 3 shows the content of macroantioxidants, estimated as the sum of HPP (hydrolyzable polyphenols) and NEPA (non-extractable proanthocyanidins) of the juice residues evaluated from the juice industry. The highest concentrations of macroantioxidants are evident in the BRS Magna (1st cycle) samples - final stage with 610.7 mg/100g dry matter, followed by Isabel Early + BRS Violet (1st cycle) - final stage containing 570.1 mg/100g dry matter and the Isabel Early variety (1st cycle) - final stage with the non-extractable polyphenol content of 552.9 mg/100g dry matter present in the bagasse evaluated. All analyzes were conducted in triplicate and the results presented with averages followed by the standard deviation.

DISCUSSION

The results shown confirm the findings of Cataneo *et al.* (2008), Lopes (2013) and Jacques *et al.* (2014) for grape residues. For Cataneo *et al.* (2008), the content of total extractable polyphenols extracted from "Couderc 13" grape residue varied from 109.64 mg GAE/100g to 207.79 mg GAE/100g; for the "Pinot gris" grape residue variety the polyphenol content ranged from 370.16 mg GAE/100g to 420.61 mg GAE/100g. In the analysis conducted by Lopes (2013), the "Concord" grapes residue and the total extractable polyphenols content were evaluated in the range of 257.2 mg GAE/100g to 339.7 mg GAE/100g of residue. In a study evaluated by Jacques *et al.* (2014), the total extractable polyphenol content for grape residue of the "Cabernet franc" variety was 1086 mg GAE/100g sample. These authors also associated antioxidant activity with presence of phenolic substances. Several studies have demonstrated that there is a significant correlation between antioxidant capacity of a fruit and its amount of polyphenol (Melo *et al.,* 2008). Postingher (2015) studied "Isabel" and "Bordô" (*Vitis labrusca* L.) grape

residues and found, in terms of concentration of polyphenols, values ranging from 80.17 mg GAE/100g to 122.39 mg GAE/100g. In a research conducted by Llobera & Cañellas (2007), with grape residue of "Manto negro" variety (*Vitis vinifera* L.), it found average contents of phenolic compounds extracted sequentially with 50% methanol and 70% acetone ($v.v^{-1}$) between 2.63 to 11.6 g GAE/100 g dry weight of the sample. In an evaluation by Soares *et al*. (2008), the total extractable polyphenol content found for "Isabel" and "Niágara" grapes was 196.83 and 183.04 mg/100g bark, respectively. In studies evaluating pulp and grape residue separately, Katalinic *et al*. (2010) and Lutz *et al.* (2005) reported higher contents of total extractable polyphenols in bagasse than in pulps of grapes, because the seed present in the bagasse is an important source of flavonoids (Vedana *et al.,* 2008).

Ruberto *et al.* (2007) evaluated the antioxidant activity of the extracts of the phenolic compounds of five grape residue of the *Vitis vinifera* species, determined an EC_{50} variation between 0.014 and 0.038 mg/mL in the DPPH radical sequestration test. In a study conducted by Silva (2010), it was verified that the "Syrah" variety showed the highest antioxidant activity in relation to the other tested samples, with EC_{50} value calculated in 1.09 µg/mL. Rubilar *et al*. (2007) in their study determined an EC_{50} value of 0.2 mg/mL for an extract obtained from grape residue of the "Cabernet sauvignon" variety. Anastasiadi *et al.* (2010), evaluating red grape varieties ("Mandilaria" and "Voidomatis") of *Vitis vinifera*, observed average values ranging from 10.9 to 14.4 µg/g of extract. Postingher (2015) evaluated the antioxidant activity by the DPPH method of the "Isabel" and "Bordô" (*Vitis labrusca* L.) grape residues, with values ranging from 0.46 mg/mL to 0.70 mg/mL. The comparison of results obtained by Ruberto *et al.* (2007), Silva (2010), Rubilar *et al.* (2007) and Anastasiadi *et al.* (2010) for residues of different grape species suggests that not only the grape variety interferes in antioxidant potential of the sample, but also harvesting period, cultivation form, soil, among other factors (Sun *et al.,* 2001). In this study, comparing BRS Magna (1st cycle) - final stage, resulting from cycle of first semester of 2015, with corresponding residue of same variety referring to the cycle of the second half BRS Magna (2nd cycle) - In the final stage, the antioxidant profile of two samples in the different cycles of year did not show any significant difference, as was observed in the total extractable polyphenols content, indicating a close relationship between polyphenol content present in food matrix and antioxidant sample profile. Thus, this result aligns with values found for analysis of total extractable polyphenols in the cited variety, where polyphenol content in different periods of the year was also considered.

According to Mazza (1995) the content of phenolic compounds in juice varies according to the variety of grape, considering maturity, regions and periods of cultivation. Abe *et al.* (2007) observed that there is a positive correlation between content of phenolic compounds and grape antioxidant capacity. As it is the raw material to produce wines and juices, it is important to know the phenolic compound content of grapes, since these can influence in quality of final products. The more intense color of grape, the more interesting it becomes from the functional point of view, since dark grapes presented higher content of phenolic compounds and antioxidant. The evaluation of the grape antioxidant activity variety, determined by the ABTS method, analyzed that grape juice elaboration presented similar antioxidant activity values in two stages of production, except BRS Magna (1st cycle) - initial and final stages. The BRS Magna variety (1st cycle) - early stage and Isabel Early + BRS Violet (1st cycle) - initial stage stood out with higher values in the cycle of the first semester of 2015. The BRS Magna variety (2nd cycle) - final stage, referring to the cycle of the second semester in the same year, also presented high antioxidant potential in comparison with the other. According to Cataneo *et al.* (2008), the antioxidant potential of the agroindustrial residue of the "Couderc 13" and "Pinot gris" grapes determined by the ABTS method were, on average, 463.46 µM TEAC/g in the "Pinot gris" variety and 98.92 µM/g for the "Couderc 13" variety. Soares et al. (2008) investigated the residues of two grape varieties ("Isabel" and "Niágara") and, based on the ABTS method for determination of antioxidant activity, found TEAC values of 89.22 µM/100g for "Isabel" and 157.31 µM/100g for the "Niágara" grape extract. According to Melo (2010), the values of antioxidant activity equivalent to trolox for the ethanol extract from the bagasse of six different grape varieties (Pinot noir, Petit verdot, Cabernet sauvignon, Verdejo, Isabel and Moscato) ranged from 69.43 to 511.97 µM trolox/g residue. In a study by Rockenbach *et al.* (2011), the evaluation of the antioxidant activity by the ABTS method for red grape residue (*Vitis vinifera* L. and *Vitis labrusca* L.) corresponding to the varieties Cabernet sauvignon, Merlot, Bordeaux and Isabel, pointed to the grape residue's values ranging from 193.36 µM TEAC/g to 485.42 µM TEAC/100g of the sample.

In an earlier study on red grape pomace of the "Regente" and "Pinot noir" varieties found values of 419 µM TEAC/g and 477 µM TEAC/g, which were obtained using the ABTS method to evaluate antioxidant activity of residues researched (Rockenbach *et al.,* 2007). The expressive variation of antioxidant activity by different methods suggests that the phenolic compounds of these residues exert antioxidant activities by different mechanisms of action, depending on the polarity of the reaction medium (Melo *et al.,* 2011). The ABTS method is widely used to test food extracts in various types of fruits because it presents advantages over other methods, since it can be used for both water soluble and liposoluble samples (Lima, 2008). According to the expressed results, the content of macroantioxidants stands out in grape residues corresponding to the final stage of residue obtaining process. In this way, it is predicted that content of non-extractable polyphenols is associated with content of polyphenolic compounds found primarily in bark and grape seeds (Monrad *et al.,* 2010). The levels of proanthocyanidins (condensed tannins) in grapes, as well as other phenolic compounds, vary with type of soil, year of harvest, caste to caste, climatic conditions and way of conducting the strains (Correia, 2014). According to Gil *et al.* (2000) and Vitaglione *et al.* (2008), an appreciable portion of hydrolysable polyphenols (hydrolysable tannins) can be observed in fruits, especially strawberries, grapes, pomegranates, peaches, cherries, plums and mangoes, which were analyzed in aqueous organic solvents. In a paper prepared by Pérez-Jiménez *et al*. (2013), some food of plant origin varieties (cereals, fruits, nuts and legumes) were evaluated in order to determine the content of non-extractable polyphenols in various foods. An approximate estimate of the content of hydrolyzable polyphenols and proanthocyanidins non-extractable was determined based on the organic-aqueous extraction method for total polyphenol content of food matrix studied. As observed, the content of hydrolyzable polyphenols for fruits, such as onion, acerola and cashew, determined in

mg/100g dry matter, were respectively 410 mg/100g dry matter; 390 mg/100g dry matter; 1210 mg/100g dry matter. For analysis of proanthocyanidins, the content determined for dry fruit samples, such as açai and banana, corresponded to 1210 mg/100g and 980 mg/100g dry matter, respectively. The analysis of extractable polyphenols (EPP), hydrolyzable polyphenols (HPP) and non-extractable proanthocyanidins (NEPA) in various types of fruits and nuts according to Pérez-Jiménez *et al.* (2013) showed that the contribution of macroantioxidants corresponds to 60 and 90% of the total content of polyphenols and therefore represents the largest fraction of these dietary antioxidants in the food matrix (Pérez-Jiménez *et al.,* 2013). Evaluating the content of two main types of macroantioxidants (non-extractable proanthocyanidins and hydrolyzable polyphenols) in specific foods identified by Pérez-Jiménez *et al.* (2014), the results for content of non-extractable polyphenols for red grapes of 146 mg/100g dry matter were observed. In analysis for other red fruits, such as açai, apple pomace and cranberry pomace, the work conducted by Pérez-Jiménez *et al.* (2013), considered for the content of non-extractable polyphenols values between 1.240 mg/100g of dry matter; 37-43 mg/100g fresh matter; 18-23 mg/100g of fresh matter; 1.685 mg/100g of fresh matter, respectively, for the red fruits researched. Rufino *et al.* (2010) in the analysis of residues of tropical fruits, acerola and cashew, obtained at the Experimental Station of Embrapa Tropical Agroindustry, Pacajus-CE, found results for hydrolysable tannins or hydrolyzable polyphenols values of 12.1 $g.kg^{-1}$ of dry matter for cashew and acerola were determined 3.9 $g.kg^{-1}$ of dry matter. In evaluation of condensed tannins or non-extractable polyphenols, the content of 52.0 g. Kg^{-1} of dry matter was found for cashew and for acerola no values were detected for the content of condensed tannins. In summary, this work provides new nutritional data on the composition of tropical fruits - acerola and cashew - that presented a high antioxidant activity due to the combination of high concentrations of extractable polyphenols and non-extractable polyphenols.

In more recent research, Camacho *et al.* (2018) evaluated the content of extractable polyphenols and non-extractable polyphenols in some tropical fruit varieties. According to obtained data, the content with higher content of polyphenols extractable for different tropical fruits was reported for camu-camu and acerola, followed by açai, tropical blackberry, murta and puçá-preto, with values varying from 1.176 mg/100g to 868 mg/100g of fresh matter. The highest concentrations of non-extractable polyphenols were reported for banana, blackberry and cashew, followed by acerola, with contents ranging from 980 mg/100g to 390 mg/100g dry matter. Thus, the content of extractable and non-extractable polyphenols determined as a result of the present study for grape residues, can be demonstrated as to be equivalent to results found in the literature. As can be observed, the awareness of the total intake of polyphenols in these foods, including the levels of extractable polyphenols and non-extractable polyphenols, is essential for a better understanding of nutritional properties of dietary polyphenols. However, current literature data on the ingestion of polyphenols are limited to EPP (Mink *et al.,* 2007; Zamora-Ros *et al.,* 2010).

Conclusions

The results reveal that grape pulp formed by bark and seeds from juice processing industry originating from the São Francisco valley is an important source of phenolic compounds and macroantioxidants. The high amounts of phenolic compounds and macroantioxidants compounds present in the bagasse can transform them into high value-added products with the potential to contribute to both human health and food preservation.

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